Some recent theoretical results on amorphous packings of hard spheres

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The aim of this paper is to review and discuss qualitatively some results on the properties of amorphous packings of hard spheres that were recently obtained by means of the replica method. The theory gives predictions for the equation of state of the glass, the complexity of the metastable states, the scaling of the pressure close to jamming, the coordination of the packing and the pair correlation function in any space dimension d. The predictions compare very well with numerical simulations in $d = 2, 3$. The asymptotic predictions for $d \to \infty$ are within the rigorous bounds. The theory can be extended to binary mixtures and to hard core potentials with an attractive tail or square well.

The study of amorphous packings of hard spheres is relevant for a large class of problems, including liquids, glasses, colloidal dispersions, granular matter, powders, porous media, etc. and a large amount of numerical and experimental data is available in the literature [1–17]. Moreover, the problem of sphere packing is related to many mathematical problems and arises in the context of signal coding and of error correcting codes, therefore it has been investigated in detail by the information theory community [18, 19]. Nevertheless, a satisfactory characterization of the amorphous states of a system of identical hard spheres is not yet available and in particular the question whether a glass transition exists in finite dimension is still open. From a rigorous point of view, for space dimension $d > 3$ only some not very restrictive bounds on the maximal density have been obtained, and in particular it is still unclear whether the densest packings for $d \to \infty$ are amorphous or crystalline.

Recently, a quantitative description of the glass transition in structural glasses has been obtained by means of the replica trick [20–25]. This method was successfully applied to Lennard-Jones systems [20–23] and, more recently, to hard spheres in $\mathbb{R}^d$ [24–26], on the Bethe lattice [27], and on the hypercube [28]. In this approximation the glass transition turns out to be similar to the 1-step replica symmetry breaking (1RSB) transition that happens in a class of mean-field spin glass models and indeed the replica strategy described above was inspired by the exact solution of these models [29–32].

In this paper I review these results, for the case of hard spheres in $\mathbb{R}^d$, without discussing the replica method, for which the reader can refer to the original papers [20–22, 25, 26]: here I will discuss in details the limits of the theory and how it compares with numerical results. As a matter of fact, despite the strong idealizations involved in the theory, the agreement with numerical data is surprisingly good.

I. WHAT IS AN "AMORPHOUS PACKING"?

In this section we will try to define "amorphous packings" of hard sphere systems and in particular the "random close packing" density, i.e. the maximum density of amorphous packings. We will see that there are difficulties in the theoretical definition of this concept that allow only to define it *approximately*. The usual way to estimate this quantity in experiments or numerical simulation is to compress the system according to some protocol: e.g. in numerical simulations the particle diameter is slowly increased during a molecular dynamics run, or in experiments particle are thrown randomly in a box and the box is subsequently shaked [1–15]. The density of the system increases with time and usually approaches a value of $\varphi_{RCP} \sim 0.64$. However the precise value of the latter quantity is found to depend in a non trivial way on the details of the experimental protocol. Then, to find a theoretical estimate of φ_{RCP} we will have to refer to some idealization. For concreteness we will discuss the problem in $\mathbb{R}^3$ but the discussion applies to any space dimension.
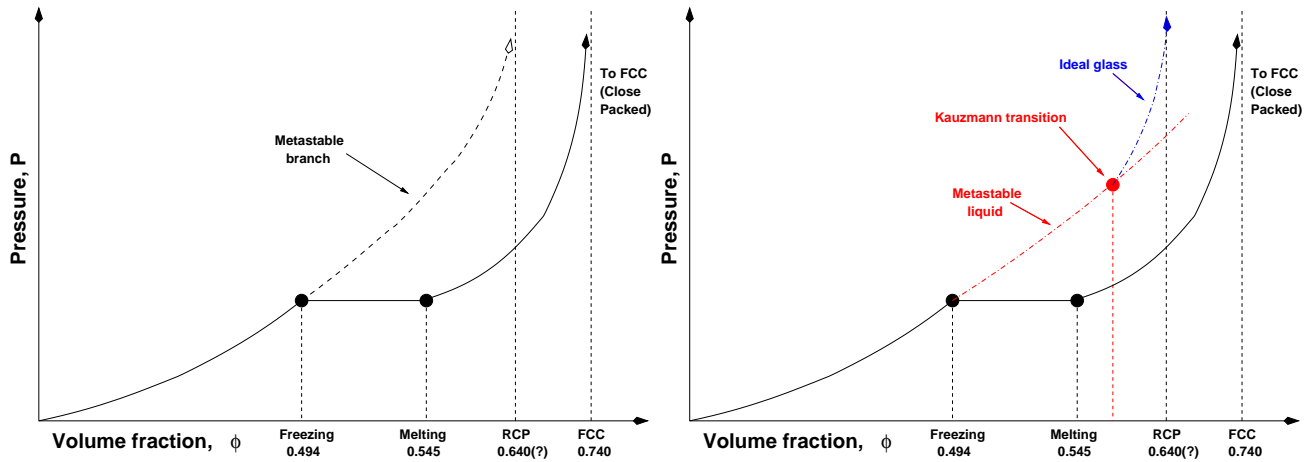
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FIG. 1: Schematic phase diagram of hard spheres in $\mathbb{R}^3$. (Left) Continuation of the liquid equation of state in the metastable region. (Right) Expected behavior in presence of a thermodynamic glass transition.

A. The fate of the liquid above freezing: a naive definition of random close packing

The equilibrium phase diagram of hard spheres in $\mathbb{R}^3$ is sketched in Fig. 1, where the density is reported as a function of the *packing fraction* $\varphi = \rho V_d(D/2)$, D being the diameter of a sphere and $V_d(r)$ the volume of a d-dimensional sphere of radius r, so that φ is the fraction of volume covered by the spheres. At low density the system is in a liquid phase (as defined e.g. by the low density virial expansion); the maximum possible density is realized by the FCC lattice. A first order phase transition between the liquid phase and the FCC crystal phase is found by numerical simulations.

The first naive idea to define amorphous states of hard spheres at high density is to assume that the liquid phase can be continued above the freezing density φ_f and to look at its properties at large density. For instance one can choose a functional form that represents well the equation of state of the liquid below φ_f (e.g. the Carnahan-Starling or Percus-Yevick equation of state [33]) and assume that it describes the liquid phase also above φ_f. On increasing the density the pressure of the liquid increases as the average distance between particles decreases: one may expect that it diverges at a point where the particles get in contact with their neighbors, and the system cannot be further compressed. Then one can call this point *random close packing density* (RCP), see left panel of Fig. 1.

The first objection to this proposal is that an intrinsic stability limit of the liquid (a spinodal point) might exist at a density above φ_f due to thermodynamic or kinetic reasons. A thermodynamic spinodal is likely not to be there and any reasonable continuation of the liquid equation of state do not predict such an instability (manifested e.g. by an infinite compressibility). A kinetic spinodal, related to the existence of the crystal [34], could instead exist, at least in monodisperse systems. This would imply the impossibility of reaching amorphous jammed states if the compression rate is not very high. We will assume in the following that the metastable liquid can be compressed as slow as wished avoiding crystallization. This is not a very good assumption for monodisperse systems but seems to be more close to reality for a suitably chosen binary mixtures. This point requires a better investigation, e.g. following the analysis of [34], and we will not discuss it further here.

A second objection is that in presence of a first order phase transition the continuation of one phase into its metastable region is not well defined due to the appearance of essential singularities at φ_f. Many possible continuations of the low density equation of state above φ_f are possible: this means that the properties of the "liquid" above φ_f will depend on the history of the sample, much as it happens for the hysteresis of a ferromagnetic system. This means that, even neglecting crystallization, the definition of RCP above is not precise from a theoretical point of view. Nevertheless, the ambiguity is expected to be exponentially small in the distance from φ_f, and as the distance between φ_f and the maximum density φ_{FCC} is not so large, one might expect to obtain a meaningful result in this way. And indeed the difference between different possible continuation of the liquid equation of state (e.g. Carnahan-Starling, Percus-Yevick, Hypernetted Chain) is of the order of 10% above φ_f.

The main problem with this definition is that all these equations predict a divergence of the pressure at unphysical large values of φ: e.g. the CS equation predicts $\varphi_{RCP} = 1$ which is clearly wrong since it is larger than the FCC value and moreover implies that the available volume is completely covered by the spheres. Thus this idea is definitely too naive and we have to resort to something more refined.

B. The ideal glass transition: a (still naive) definition of RCP

A way out of this contradiction is to assume the existence of a thermodynamic glass transition in the *metastable* liquid branch of the phase diagram. Such a transition can be expected for various reasons but we will not try to justify it: we will simply assume that it is there and investigate the consequences of such an assumption.

So let us assume again that the liquid phase can be continued above φ_f and neglect the (small) ambiguity in its definition due to its intrinsic metastability with respect to crystallization. We assume that at a density φ_K a *thermodynamic glass transition* (sometimes called *ideal glass transition*) happens. The transition is signaled by a jump in the compressibility of the system. A simple qualitative argument to explain this is the following: in the dense liquid phase particles vibrate on a fast time scale in the cages made by their neighbors, while on a much larger time large scale cooperative relaxation processes happen (*structural relaxation*). If we change the density by $\Delta\varphi$ the pressure will instantaneously increase by a ΔP_0; very rapidly the average size of the cages will decrease a little due to the increase in density and the pressure will relax to a value $\Delta P_f < \Delta P_0$. Then, on the time scale of structural relaxation, the structure will change to follow the change in density and the pressure will relax further to a value $\Delta P_\infty < \Delta P_f$. At the glass transition the latter relaxation is frozen as the corresponding time scale becomes infinite. Thus, in the glass phase the increase in pressure following a change in density will be larger than in the liquid phase, leading to a smaller compressibility $K = \varphi^{-1}(\Delta\varphi/\Delta P)$.

The schematic phase diagram that we expect in presence of a glass transition is in right panel of Fig. 1. It is evident that the existence of a glass transition can cure the paradoxical behavior of the pressure of the liquid, that seems to diverge at a density bigger than the FCC density. Then we can define the RCP density as the point where the pressure of the *glass* diverges.

Still this definition of RCP in unsatisfactory for two reasons. The first is that the ambiguity in the definition of the liquid equation of state due to its metastability affects also the glass: so the glass equation of state will be *theoretically* not well defined, with an ambiguity of the order of 10%, depending on the equation of state one chooses to describe the liquid. Moreover, the existence of the crystal means that one can construct configurations of the system representing mixtures of the crystal and the glass states; such configurations will have an arbitrary degree of local order and will span the whole range of densities between the density of the glass and that of the crystal: explicit examples have been constructed in [12]. It is very difficult to define an "order metric" to quantify the order in a given configuration of a large system. Thus *on a practical ground* it is very difficult to distinguish a "pure glass state" from a mixture of glass and crystal. To resume, the existence of the crystal poses both theoretical and practical difficulties in defining RCP as the point where the pressure of the equilibrium glass diverges.

A second difficulty is the following. The glass transition, in the standard picture coming from the analysis of mean field models, is due to the appearance of many metastable states: in the case of hard spheres this means that we expect that, in addition to the stable glass states corresponding to the equilibrium glass, we will have many *metastable packings*. These packings can be described as follows: in the equilibrium liquid at a given (high) density $\varphi < \varphi_K$ the particles will vibrate around local stable structures, that are visited subsequently on the scale of the structural relaxation. If we now "artificially" froze the structural relaxation and compress the system, the pressure will increase faster than if the structure is allowed to relax for the same reason as above: the system will be forced to reduce the size of the cages to respond to a change in density. Then the pressure will diverge at the point where the particles get in contact with their neighbors and the average size of the cages is zero. In this way we can produce *jammed* configurations in a whole range of densities $\varphi < \varphi_{RCP}$ [12–15]. Experimentally or numerically this can be done by compressing fast enough in order to disallow the system to relax the structure during compression. And it is clear that, as the time scale for structural relaxation is expected to diverge on approaching φ_K, at some point it will fall beyond any experimentally accessible time scale and necessarily the system will be frozen into a metastable state. Thus the *ideal* glass states are likely to be unobservable in practice: one will observe instead a *nonequilibrium* glass transition to a state that, again, will depend on the experimental protocol.

To summarize, the difficulties in the definition of the random close packing are mainly due to *metastability*, either of metastable glass states with respect to the ideal glass states, or of the whole glass states with respect to the crystal. Thus, in the following we will *assume* the idealized phase diagram given in Fig. 1, neglect the existence of the crystal and try to compute properties of the pure ideal glass state, and possibly also of metastable glass states. We will see that even in this "zeroth order" approximation we can obtain a very good agreement with numerical simulations. Moreover, we will consider the limit $d \to \infty$ in which the ambiguities related to metastability are expected to be much smaller. We believe that it is possible that in this limit the theory is exact.

The method we used has been described in [25, 26]. In an extended version of this paper we will present a simpler derivation, explain how crystallization is removed in the theory and qualitatively discuss the effect of metastability.
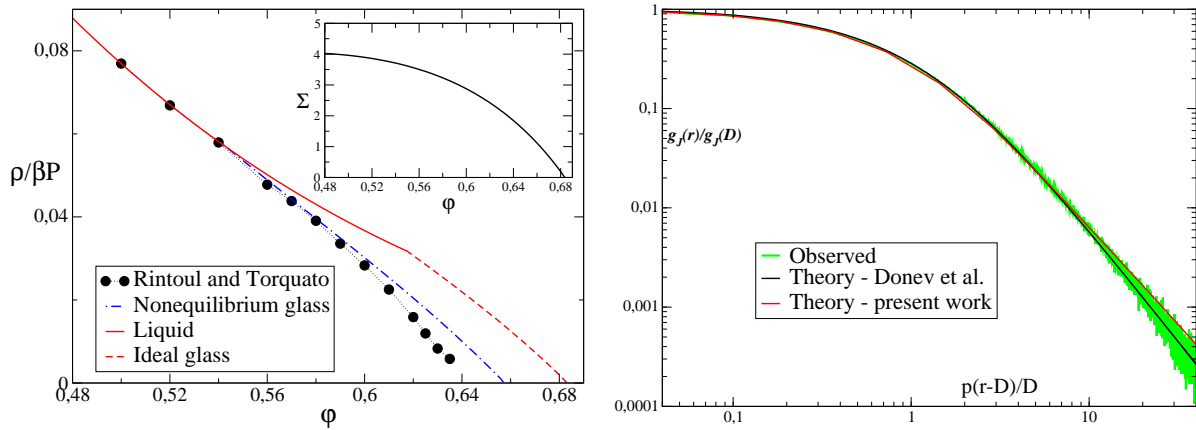
FIG. 2: (Left) Equation of state in $d = 3$ using the Carnahan-Staling equation of state to describe the liquid. The inverse of the reduced pressure $\beta P/\rho$ is reported as a function of φ. The ideal glass transition density is $\varphi_K = 0.62$ and the random close packing density is $\varphi_{RCP} = 0.68$. The metastable state reported in the figure correspond to a jamming density $\varphi_J = 0.658$. Numerical data from [10] are reported for comparison. (Inset) Complexity as a function of the jamming density for $d = 3$. (Right) Scaled correlation function $g_J(r)/g_J(D)$ close to $r = D$. The theory is compared with numerical data from [14].

C. On the protocol dependence of the random close packing density

Generally speaking, we can use a given algorithm to produce jammed configurations of hard spheres: the case we discussed above corresponds, for instance, to a molecular dynamics simulation during which the system is compressed at a given rate. The algorithm will stop when the system is jammed: the final density will be a random variable depending on the initial data and possibly on some randomness built in the algorithm itself. We can define the probability $\mathcal{P}(\varphi_J)$ of reaching a final density φ_J: it will be the product of the *density of states* $\rho(\varphi_J)$, i.e. the number of jammed configurations with density φ_J, times the probability $\beta(\varphi_J)$ that the algorithm finds a particular configuration with density φ_J. The former quantity depends only on geometrical properties of the configuration space of hard spheres, while the latter encodes the properties of the algorithm [15].

We can compute the *complexity* $\Sigma(\varphi_J) = \lim_{N\to\infty} N^{-1} \log \rho(\varphi_J)$ for the "amorphous states" defined above. This quantity is reported in Fig. 2. It vanishes linearly at φ_{RCP} giving an exponential distribution of the jammed states, $\rho(\varphi_J) \sim \exp[N(\varphi_J - \varphi_{RCP})]$. However the quantity $\beta(\varphi_J)$ is also expected to scale as $\beta(\varphi_J) \sim \exp[Nb(\varphi_J)]$; the resulting $\mathcal{P}(\varphi_J)$ will be strongly peaked around a given value φ_J^* – the maximum of $\Sigma(\varphi_J) + b(\varphi_J)$ – [35], which however might depend on the particular algorithm through the function $\beta(\varphi_J)$, giving rise to the protocol dependence observed in experiments, see [15] for a detailed discussion of this important issue. However, the value φ_{RCP} defined as the point where $\Sigma(\varphi_J)$ vanishes is a property of the system that does not depend on the algorithm (at least if one accepts the idealizations discussed in the previous subsection, i.e. if one neglects the existence of the crystal).

II. RESULTS

A. Equation of state of the glass

The only input of the theory is the entropy of the liquid, $S(\varphi)$. As discussed above, this quantity is not well defined above the freezing density and we have to choose an expression which describes well the liquid below φ_f and extrapolate above φ_f.

d=1 - In dimension $d = 1$ we do not expect any glass transition. The entropy can be computed exactly and is given by $S(\rho) = 1 - \log \rho + \log(1 - \rho D)$: it diverges at the close packing $\rho D = 1$. Indeed we find no glass transition.

d=2 - In $d = 2$ we can use either the Henderson expression for $S(\varphi)$ [36], or the improved expression of Luding [37], with very small quantitative differences. Again we find no glass transition, consistently with the numerical simulations of [38], but we find a glassy solution which never becomes stable. The properties of the amorphous states seem to be similar to the one observed in the numerical simulations of [39] (see below). However in $d = 2$ the hard sphere liquid has very peculiar properties so this case deserves further investigation.

d=3 - In $d = 3$ we used the Carnahan-Starling expression [33] for the entropy, which reproduces very well the numerical data for the equation of state. We predict a glass transition density $\rho_K \sim 0.62$ in good agreement with numerical results. The pressure of the equilibrium glass diverges at $\varphi_{RCP} \sim 0.68$. We can also compute the equation of state of the metastable (or nonequilibrium) glasses. The latter are labeled by their jamming density φ_J which is the density at which the pressure of the metastable glass diverges. We find a whole distribution of metastable glasses with jamming densities $\varphi_J < \varphi_{RCP}$. A comparison with numerical data is in Fig. 2: the comparison suggests that the value $\varphi_J \sim 0.64$ observed in numerical simulation correspond to the jamming density of a *metastable* state in which the system is frozen due to the finite accessible time scale. The *ideal* value of $\varphi_{RCP} \sim 0.68$ would be reached only by an infinitely slow compression (if crystallization is avoided).

d→ ∞ - The entropy of the hard sphere liquid for $d \to \infty$ was computed in [40, 41] in two different ways, and in both cases it was found that $S(\varphi)$ is given by the ideal gas term plus the first virial correction (i.e. by the Van der Waals equation), $S(\varphi) = 1 - \log \rho - 2^{d-1}\varphi$ with exponentially small correction in $d \to \infty$. Using this expression we find that both φ_K and φ_{RCP} scale asymptotically as $d \log d/2^d$, with $\varphi_{RCP} - \varphi_K \sim d/2^d$. We can compare this prediction for the maximum density of amorphous packings with the best available bounds on the density of crystalline packings. Unfortunately, the best lower bound for periodic packings is the Ball bound $\varphi > d/2^d$, while the best upper bound is the Blichfeldt's one, $\varphi < 2^{-d/2}$ [18, 19]. Our result for φ_{RCP} lies between these bounds so we cannot give an answer to the question whether the densest packings of hard spheres in large d are amorphous or crystalline. Hopefully better bounds on the density of crystalline packings will address this question in the future. Recent related work appeared also in [42].

B. Scaling close to jamming

We can derive asymptotic relations for the behavior of the metastable states at $\varphi \to \varphi_J$ (the equilibrium glass corresponds to the particular case $\varphi_J = \varphi_{RCP}$).

The complexity $\Sigma(\varphi_J)$, that represents the logarithm (per particle) of the number of jammed structures with density φ_J, is given by

$$\Sigma(\varphi_J) = S(\varphi_J) - d \log \left[\frac{\sqrt{8}}{2^d \varphi_J Y(\varphi_J)} \right] + \frac{d}{2} , \tag{1}$$

where $Y(\varphi_J)$ is the value of the pair correlation at contact. It is reported in Fig. 2 for $d = 3$. Note that unfortunately we cannot investigate the stability of the *metastable* packings so we do not know the minimal value of φ_J.

The entropy of a metastable glass is found to diverge as

$$s(\varphi, \varphi_J) \sim d \log(\varphi_J - \varphi) \tag{2}$$

close to φ_J, so that the (reduced) pressure diverges as

$$p(\varphi, \varphi_J) = -\varphi \frac{ds(\varphi, \varphi_J)}{d\varphi} \sim \frac{d \ \varphi_J}{\varphi_J - \varphi} . \tag{3}$$

It is important to remark that the corrections to the leading order seem to be quite large, as observed in numerical simulations.

C. Correlation function

The most interesting results on the scaling close to φ_J are obtained by investigating the pair correlation function $g_J(r)$ of the spheres in the packing. This quantity can be (partially) computed within our theory: the details are in [25]. We find that $g_J(r) = g(r)[1 + \delta g_J(r)]$, where $g(r)$ is the pair correlation of the liquid and $\delta g_J(r)$ is a correction which is large for $r - D \lesssim \sqrt{\varphi - \varphi_J}$. In this region we have, for $\varphi \to \varphi_J$:

$$\frac{g_J(r)}{g_J(D)} = \Delta_0 \left[\frac{\sqrt{\pi}}{2} \frac{p(\varphi, \varphi_J)(r - D)}{D} \right] , \qquad \Delta_0(u) = 2 \int_0^\infty dy \, y \, e^{-y^2 - 2uy} = 1 - \sqrt{\pi} u e^{u^2} (1 - \mathrm{erf}(u)) . \tag{4}$$

In Fig. 2 we report numerical data from [14] on the delta-peak contribution for a packing in $d = 3$ with $\varphi_J \sim 0.64$ and $\varphi_J - \varphi \sim 10^{-12}$. We see that our result, given by Eq. (4) for $\varphi_J = 0.64$, perfectly agrees with the data. Unfortunately there are some contributions to $g_J(r)$ that we still are not able to compute: we expect these corrections to be responsible for the power law divergence of $g_J(r)$ for $r \to D$ and for the splitting of the second peak as described e.g. in [14].
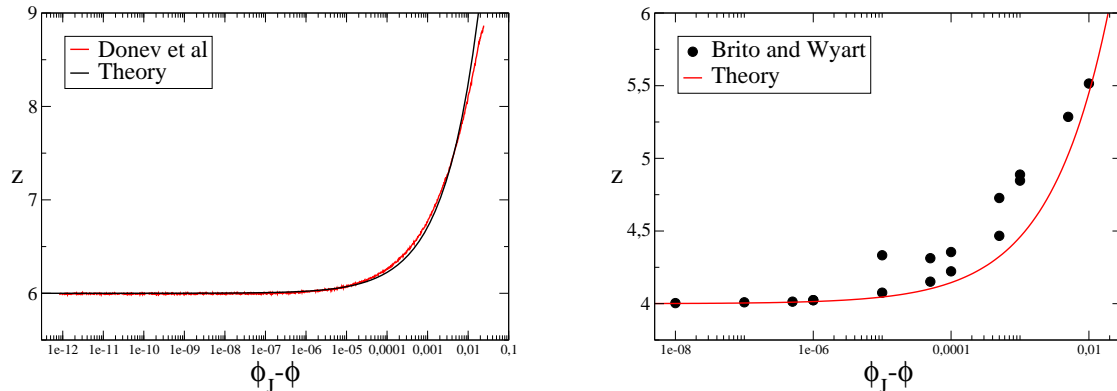
FIG. 3: Number of contacts. (Left) Data from [14] in $d = 3$ and $\varphi_J \sim 0.64$. The theory predicts $z = 6 + 20\sqrt{\varphi_J - \varphi}$. (Right) Data from [39] in $d = 2$ and $\varphi_J \sim 0.83$. The theory gives $z = 4 + 14.5\sqrt{\varphi_J - \varphi}$.

D. Number of contacts

For $\varphi \to \varphi_J$ there is a shell of width $\sqrt{\varphi_J - \varphi}$ around a given particle where the probability of finding other particles is very high, as expressed by the correction $\delta g_J(r)$. These particles will become *neighbors* of the particle in the origin at $\varphi = \varphi_J$, and their number is finite as the integral of $\delta g_J(r)$ on this shell is finite. The integral of $g_J(r)$ on a shell $D \leq r \leq D + O(\sqrt{\varphi_J - \varphi})$ gives then the average number of contacts for $\varphi \to \varphi_J$, which turns out to be $z = 2d[1 + A(\varphi_J)\sqrt{\varphi_J - \varphi}]$, where the coefficient $A(\varphi_J)$ can be explicitly computed. For $\varphi_J - \varphi$ finite but small this number can be interpreted as the number of particles that collide with the particle in the origin during a finite but long time τ [14, 39]. The result is compared with numerical data in Fig. 3. Remarkably it compares well with simulations also in $d = 2$, indicating that the (unstable) glass phase we find in $d = 2$ might have some connection with bidimensional amorphous packings.

III. CONCLUSIONS

The replica method seems to be a powerful tool to investigate the properties of amorphous packings of hard spheres. Despite the idealizations involved in this approach, the results seem to compare well with numerical simulations in $d = 2, 3$. As the method works in any space dimension, it gives predictions in $d > 3$ that we hope will be tested in the future. In the limit $d \to \infty$ the method is likely to become exact and we hope that this work will stimulate new more rigorous investigations of this (and related) problems.

There are still a number of issues that have to be addressed within the theory: for instance, a full computation of the pair correlation of the glass is mandatory, and an investigation of the stability of the jammed configurations should be performed.

Work is in progress to extend the method to the case of binary mixtures, following [23]. In this case crystallization should be less relevant and more reliable prediction should be obtained, as in the case of Lennard-Jones systems. We would like also to apply the method to hard spheres with attractive potentials like Yukawa tails or square wells: for these potentials Mode-Coupling theory predicts a rich phenomenology (reentrance of the glass transition line, glass-to-glass transition, ...) [43]. Some of these results have indeed already been reproduced within a replica method similar to the one presented here [44].

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